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to

The National Toxicology Program

- Appendix 7 -

**Benzo[a]pyrene:
Environmental Distribution and
Human Exposure**

March 20, 1998

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Benzo[a]pyrene: Environmental Distribution and Human Exposure

Incomplete combustion of organic matter represents the major source of polynuclear aromatic compounds (PAH) in the environment. PAHs are found at detectable concentrations in air, water, and soil samples of all types. Concentrations are typically small, in the order of $\mu\text{g/kg}$ or ng/m^3 . Since PAHs are highly lipophilic, they accumulate in organic fatty material and therefore have the potential to concentrate in the food chain.

Of the numerous PAHs, one compound that has perhaps received the most attention is benzo[a]pyrene (BaP). It is the focus of this discussion. The International Agency for Research on Cancer (IARC) has classified BaP as *probably carcinogenic to humans -- IARC Overall Evaluation 2A* (IARC, 1983, 1986a, 1986b). BaP has been identified in both mainstream and sidestream smoke from cigarettes, cigars, and pipes; marijuana smoke; and smoke-polluted environments (IARC, 1986b). Non-occupational inhalation exposure to BaP is primarily from tobacco smoke and urban air. However, Hattermer-Frey and Travis (1991) estimate that inhalation accounts for only 2% of the total daily intake of BaP. The focus of this paper therefore concerns the environmental distribution of BaP and human exposure to BaP.

Atmosphere: Emission Sources of BaP

Osborne and Crosby (1987) cite the principal sources of BaP in the atmosphere as (1) coal- and oil-fired power stations, (2) domestic heating, (3) miscellaneous industrial processes, (4) vehicle exhausts, and (5) cigarette smoke, forest fires and volcanic activity. The yearly global emission of BaP is estimated to be about 5,000 tons, with the greatest contribution coming from coal combustion. BaP emissions in the U.S. have been estimated to be 1,260 tons/year, accounting for approximately 25% of the worldwide total (Grimmer, 1979).

As can be seen in **Table 1**, the major emission sources in the U.S. are heating and refuse burning. The percentages in **Table 1** are derived from a table presented by Grimmer (1979), reproduced herein as **Table 2**.

Since Osborne and Crosby (1987) cited cigarettes as a principal source of BaP emissions, an estimate was calculated of the tons emitted in sidestream smoke/year. This estimate is based on cigarette consumption/year in the U.S. (Tobacco Manufacturers Association, 1997), and uses the value of 147 ng/cig BaP in sidestream smoke (SS) (based on values for the 1R4F reference cigarette cited in R.J. Reynolds, 1988). **Figure 1** shows that for the years 1983-1996, the estimated emission of BaP in sidestream smoke to the atmosphere is less than 0.099 tons/year, which calculates to be less than 0.007% of the total estimated emissions in the U.S. Thus, SS is certainly not a major contributor to BaP in the atmosphere, compared to other sources.

Table 1. Percentage by source of estimated BaP emission in the United States.

Emission source	Percentage
Automotive exhaust	1.7
Heating	38
Refuse burning	45
Industrial plants	16

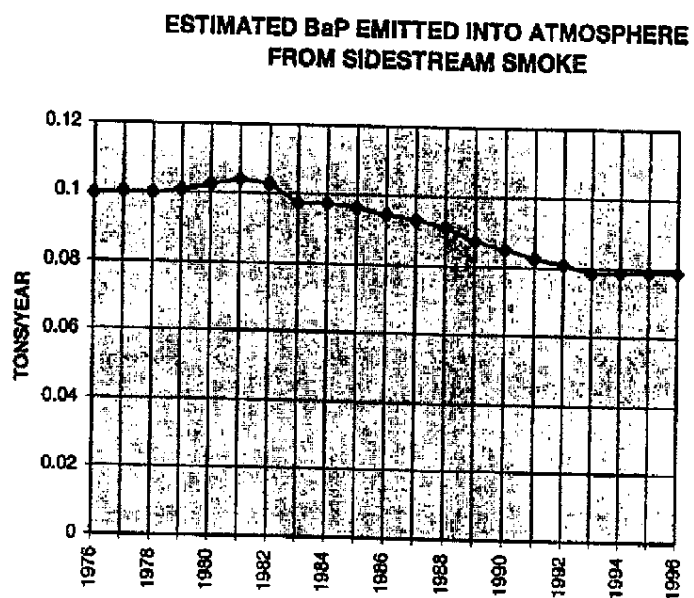
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Table 2. Estimated B(a)P emissions in the United States, after Grimmer (1979).

Source	Tons/year	Total
Vehicle exhaust		
Gas-powered cars	10	
Gas-powered trucks	12	
Diesel fuel-powered trucks and buses	0.4	
		22.4
Heating		
Coal		
Hand-stoked residential furnaces	420	
Intermediate units	10	
Coal-fired steam power plants	1	
Oil		
Low-pressure air atomizer and others	2	
Gas	2	
Wood	40	
		475
Refuse burning		
Commercial, residential, institutional and apartments	33	
Open burning		
Forest and agricultural	140	
Vehicle disposal	50	
Coal refuse fires	340	
		563
Industrial plants		
Petroleum cracking	6	
Asphalt air-blowing	<1	
Coke production	192	
		200
Total (all sources)		1260

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Figure 1.



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Occurrence of BaP in Air

The concentration of BaP in ambient air is dependent on a number of factors:

- 1) Season -- generally highest in winter and lowest in summer;
- 2) Source of emission -- industrial and transportation;
- 3) Meteorological factors;
- 4) Urban vs. rural settings; and
- 5) Geographic location (Europe vs. U.S.).

Table 3 and **Table 4** (after Pucknat, 1981) illustrates some of these factors; they are cited in the literature as being used for various calculations. The U.S. average for urban sites for the 5-year period 1966-1970 is about 2.0 ng/m³ (Pucknat 1981, p. 85). The BaP concentration range in urban air of U.S. cities as determined by various authors in recent years (published during the period 1971-1977) is 0.13 to 3.2 ng/m³ (Pucknat, 1981, p. 169). As can be seen in **Table 5**, BaP levels in European countries have historically been much higher than those reported in the U.S.; there is also a wide variation from winter to summer.

Pucknat (1981) cites a paper within a paper which reports a "safe" lifetime BaP dose for human lungs as 4.3 mg. On the basis of this value, he then states that the concentration of atmospheric BaP should not exceed 120 ng/m³. A standard BaP concentration for industrial workers was determined to be 200 ng/m³. (OSHA Workplace Exposure Limit (PEL) for coal tar pitch

Table 3. Average BaP concentrations (ng/m³) in U.S. urban and rural areas (after Pucknat (1981), Table 5.14, p. 168).

	1966	1970	1976
Urban	3.2	2.1	0.5
Rural	0.4	0.2	0.1

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Table 4. Summer-winter average of ambient BaP concentrations (ng/m³) in the air of selected cities (after Pucknat (1981), p. 169).

City	BaP (ng/m ³)
Atlanta	4.5
Birmingham	15.7
Detroit	18.5
Los Angeles	2.9
Nashville	13.2
New Orleans	3.1
San Francisco	1.3

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Table 5. Atmospheric benzo[a]pyrene concentrations (ng/m³) for various locations around the world in summer and winter (after Osborne and Crosby (1987), Table 17.1, page 302).

Location	Winter	Summer	Year
Sydney	8	0.8	1962-63
Liege, Belgium	110	15	1958-62
Ontario, Canada	15-20	1.2-18.5	1961-62
Prague	122	19	1964
Copenhagen	17	5	1956
Helsinki	5	22	1962-63
Paris	300-500		1958
Budapest	1000	32	1968
Teheran	6	0.6	1971
Belfast	51	9	1961-62
Milan	610	3	1958-60
Amsterdam	22	2	1968
	18	2	1969
	5		1970
	8		1971
Oslo	15	1	1956
Poland	130	30	1966-67
Madrid	120	0	1969-70
Stockholm	10	1	1960

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volatiles of 0.2 mg/m³ averaged over an 8-hour workshift (Final Rule, January 1989); NIOSH recommended airborne exposure limit for coal tar pitch volatiles of 0.1 mg/m³ over a 10-hour workshift; ACGIH recommendation that worker exposures, by all routes, be controlled to levels as low as can be reasonably achieved; New Jersey Hazardous Substance Fact Sheet -- Benzo(a)Pyrene -- Micromedex, Inc., 1974-1998.)

Water: Sources and Occurrences

According to a National Academy of Sciences (NAS) report (*Petroleum in the Marine Environment*, NAS 1975), about 6 million tons of petroleum hydrocarbons enter the oceans annually; the major contributors are marine transportation and runoff (urban and river). Other sources of PAHs in the oceans are coastal refineries, industrial and domestic waste, natural seeps, and atmospheric fallout. BaP levels found in water are shown in Table 6 (after Osborne and Crosby, Table 17.5, p. 307).

As one can see, the levels vary significantly depending upon the sampling location and the type of water, but in general they are rather low. This is not unexpected since PAH compounds in solution are readily adsorbed on to the surface of dust, soil or other insoluble particles. These particles will fall slowly to the bottom, and thus PAH compounds are removed from solution. The levels of BaP reported in sediments on the other hand can be rather high in the order of $\mu\text{g/kg}$ or even mg/kg of dry sample.

Table 6. BaP levels in water.

Sample	Country	BaP (ng/L)
Tap water	FRG	0.25 - 9
Tap water	USA	0.2 - 1.6
Groundwater	FRG	1 - 10
Groundwater	USA	0.2
Rainwater	FRG	4 - 80
Reservoirs	UK	0.7 - 3.8
Well water	UK	0.2 - 0.6
Well water	FRG	2 - 15
Lake Erie	USA	0.3
River Rhine at Mainz	FRG	50 - 110
River Rhine at Koblenz	FRG	10 - 60
River Thames	UK	170 - 280
River Thames	UK	4.2 - 430
River Trent	UK	5.3 - 504
River Severn	UK	1.5 - 48
Ohio River	USA	5.6
Delaware River	USA	41.1
Motorway run-off	UK	570
Domestic effluent	FRG	38
Human urine		1300
Sewage sludge	FRG	1.7 (mg/kg)

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Soil: Sources and Occurrences

The majority of investigations of PAHs in soils have been carried out by Soviet investigators between 1967-1977; these papers only reported the BaP content (Osborne and Crosby, 1987). The concentrations of BaP measured in the U.S.S.R. ranged from 0.0008 mg/kg to 200 mg/kg, with the maximum value found in the vicinity of an oil refinery. Similarly high concentrations (650 mg/kg) were measured in the area of a carbon black factory. In samples of sandy and forest soil collected in West Germany, considerably lower concentrations of BaP, ranging from 0.001 to 0.0004 mg/kg, were found. The contamination of soil can be attributed almost exclusively to emissions from combustion processes. In the majority of surface soil samples taken in Iceland, where hardly any fossil fuels are burnt, the most commonly found PAHs were not detected (detection limit for BaP, e.g., 0.02 $\mu\text{g/kg}$ soil). Soil samples taken at the Reykjavik, Iceland airport, however, were extremely contaminated, with BaP concentrations reaching 0.785 mg/kg.

"Human Exposure to Benzo(a)pyrene"

Hattemer-Frey and Travis (1991) used a multimedia transport model to evaluate environmental partitioning of BaP. Measured and predicted environmental concentrations were used to estimate the accumulation of BaP in the food chain and the subsequent extent of human exposure from inhalation and ingestion. Their results showed that the food chain is the dominant pathway of human exposure, accounting for about 97% of the total daily intake of BaP. See Table 7.

Table 7. Pathways of human exposure to B(a)P (after Hattemer-Frey and Travis, 1991).

Source	Daily intake ($\mu\text{g/day}$)	% of total daily intake
Food (total)	2.1	97
Inhalation	0.05	2
Water	0.01	1
TOTAL	2.16	100

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This value of approximately $2.2 \mu\text{g/day}$ average daily intake of BaP is in agreement with other values reported in the literature (e.g., Suess, 1976). Hattemer-Frey and Travis (1991) then went on to discuss human exposure to BaP from smoking and indoor air pollution, referencing a paper by Butler and Crossley (1979) that reportedly estimated that one cigarette delivers approximately 39 ng of BaP. Further, Hattemer-Frey and Travis used in their calculations an estimate that the average smoker smokes 20 cigarettes per day. Based on these calculations, they suggested that the smoker receives an additional 780 ng/day ($0.78 \mu\text{g/day}$) BaP from smoking. Additionally, they again referenced Butler and Crossley (1979), who reported that concentrations of BaP measured indoors (2.2 ng/m^3) were comparable to outdoor air concentrations (2.5 ng/m^3); thus, indoor activities would not substantially increase the BaP intake, since inhalation is not a major pathway of human exposure to BaP.

Mainstream smoke concentrations of 9.2 ng BaP/cigarette have been reported for the Kentucky Reference Cigarette 1R4F (R.J. Reynolds, 1988). The value for a filtered cigarette could be rounded to 10 ng BaP/cigarette. Thus, an average (1 pack/day) smoker of filtered cigarettes would be exposed to an additional $0.2 \mu\text{g/day}$ of BaP, a level which is approximately 4 times the estimated daily intake of BaP by inhalation. [See Table 8] However, one should keep in mind that more than 90% of the daily intake of BaP is derived from other sources, primarily food.

This can be examined from the perspective of the daily lung burden as described by Chen and Thilly (1996). Instead of using the value of $10 \text{ m}^3/\text{day}$ for breathing, the more widely used value of $20 \text{ m}^3/\text{day}$ will be chosen. The value of 2.5 ng BaP/m^3 as the "urban air concentration" will

Table 8. **Estimated exposure of a smoker to BaP (ng/day).**

	Cigarettes/day		
	10	20	40
1R4F filtered cigarette	100	200	400

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be used, which, as shown in **Table 9**, is probably an over-estimation of the urban air BaP concentration in the 1990s, if the downward trend has continued.

Using the formula (breathing rate/day X urban air BaP level) = ng BaP by inhalation/day, for a breathing rate of 20 m³/day X 2.5 ng BaP/m³ = 50 ng BaP/day or 0.05 µg/day by inhalation/day. The level of 0.05 ug/day by inhalation corresponds to what Hattener-Frey and Travis reported [See **Table 7**].

Examining BaP Exposure from ETS or Room-Aged Sidestream Smoke (RASS)

Attributing levels of PAH (BaP) in the air of restaurants, public rooms, etc., to ETS is difficult since other sources may be present, and other factors, such as ventilation rates, number of smokers, etc., may confound the issue. However, Grimmer (1983), under controlled conditions, reported 22 ng/m³ BaP where cigarettes were being smoked and less than 3 ng/m³ where no cigarettes were being smoked. He calculated that ETS contributed about 7 times the background BaP level. Grimmer states that "the measured concentrations of 22 ng BaP per cubic meter has to be considered as a maximum BaP concentration attainable by smoking. In practice nobody would tolerate this concentration" of smoke due to eye irritation, etc.

A 12-month inhalation study in rats using room-aged sidestream smoke (RASS) (INBIFO, data enclosed) reports the following concentrations of BaP in RASS from 1R4F cigarettes: 0.13 µg/m³ (upper limit) for the whole-body 12-month exposure group, and 0.121 µg/m³ (upper

Table 9. Average BaP concentrations (ng/m³) in U.S. urban and rural areas during 1966-1977 (after Pucknat 1981, Table 5.14, p. 168).

Location	Year		
	1966	1970	1976
Urban	3.2	2.1	0.5
Rural	0.4	0.2	0.1

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limit) for the head-only 12-month exposure group (Haussmann et al., 1998). Again, if we consider urban ambient air to contain an average of 2.5 ng/m^3 BaP, one can see that the rats in this study were exposed to approximately 50 times the level of BaP found in ambient air. The RASS concentrations in this study were approximately 100-fold higher than the maximum of the average concentrations of respiratory suspended particles (RSP) reportedly attributable to ETS (Guerin et al., 1992; U.S. EPA, 1992; Jenkins et al., 1996). Thus, if one assumes that BaP, which is in the particulate phase, tracks with RSP, then $0.13 \text{ } \mu\text{g/m}^3$ would correspond to $0.0013 \text{ } \mu\text{g/m}^3$. From the perspective of human exposure, this level of exposure would be equivalent to $0.0013 \text{ } \mu\text{g/m}^3 \times 20 \text{ m}^3/\text{day} = 0.026 \text{ } \mu\text{g/}$ or 26 ng/day , which is about half the daily level by inhalation estimated by Hattner-Frey and Travis.

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